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## A REVISION OF THE ATOMIC WEIGHT OF CADMIUM

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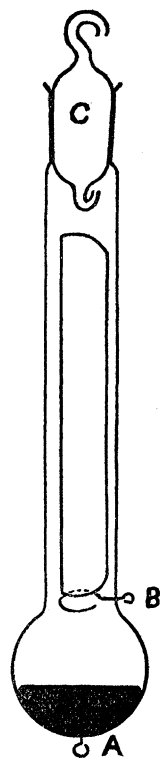
In several recent investigations by Hulett and his collaborators<sup>1</sup> concordant values have been obtained for the atomic weight of cadmium by the electrolytic deposition, in a mercury cathode, of the metal in hydrated and anhydrous cadmium sulphate and in anhydrous cadmium chloride and bromide, and by the comparison of simultaneous electrolytic deposits of cadmium and silver. The average value so obtained for the constant in question is 112.3. On the other hand, Baxter, Hines, and Frevert<sup>2</sup> had previously found a considerably higher value, 112.42, by the estimation of the halogen-content of cadmium chloride and bromide. So wide a discrepancy is disturbing and obviously needs attention. We therefore decided to repeat a portion of the work of Quinn and Hulett by analyzing anhydrous cadmium chloride through the electrolytic deposition of the cadmium in a mercury cathode.

Cadmium material was purified (1) by electrolytic deposition with a dissolving anode (yielding samples *A* and *B*), (2) by fractional precipitation with hydrogen sulphide (yielding samples *C* and *D*), and (3) by crystallization of cadmium bromide (yielding samples *E* and *F*); these operations being followed by crystallization of cadmium chloride (except in the case of sample *E* where the bromide was converted into chloride by fusion in a current of dry chlorine). Another sample (*G*) was obtained by combining the mother-liquors of the other specimens of cadmium chloride and, after crystallizing the salt, fusing the mixture in dry chlorine. In order to follow the purity of the different samples, the metal was deposited electrolytically from the mother-liquor of the last chloride crystallization in each case; and, after conversion into electrodes by fusion, it was used for the production of spark-spectra which were photographed in a Féry quartz spectrograph. Careful examination of the spectrograms in the visible and ultraviolet regions showed that some of the samples were wholly free from impurities, and that, although some of them contained traces of copper and lead, the proportions of these impurities were too small to have any perceptible effect upon the outcome. Furthermore, the analyses of the chloride showed no apparent differences between the different samples. On the whole, crystallization of cadmium bromide seemed to be the most rapid and efficient method of purifying cadmium material.

For the electrolytic deposition of the metal the special form of cell shown in the figure was designed. In this cell both the cathode *A* and the anode *B* were fused into the glass and weighed with the cell, in order that any metal dissolved from the anode during electrolysis might immediately be deposited upon the cathode. This made it possible to electrolyze the chloride solution directly without previous removal of the chlorine. Another advantage of this form of cell lies in the possibility of introducing bodily the boat in which the salt was fused preparatory to weighing, so that no quantitative transference of solution was necessary. The mercury and the amalgams were prepared for weighing by washing with water and alcohol and drying in a high vacuum. Spurting of the amalgams out of the cell during the drying was prevented by the specially constructed stopper *C*, which was always weighed with the cell.

Blank determinations in which hydrochloric acid solutions were electrolyzed showed that the cell with a charge of mercury could be depended on to remain constant in weight. Furthermore, no evidence could be found of appreciable oxidation of the amalgams.

The experimental procedure of an analysis was as follows: The cadmium chloride, in a quartz boat contained in a quartz tube, was heated in a current of pure dry hydrochloric acid gas, gently at first so as to expel as much as possible of the water at a low temperature, but finally for some minutes at the fusing-point. After the tube had been allowed to cool, the hydrochloric acid was displaced by pure dry nitrogen, which was in turn displaced by dry air. Then the boat was transferred to the weighing bottle, in which it was originally weighed, by means of a 'bottling apparatus,'<sup>3</sup> without exposure to moisture, and weighed. Next the boat was inserted in the cell, in which it was supported upon the anode. The weighing bottle was rinsed, and the rinsings were used to dissolve the salt in the cell. For the purpose of retaining spray formed during the electrolysis, a column of bulbs, which had been ground into the mouth of the cell, was inserted. Electrolysis was then commenced, at first with a current of about 0.5 ampere. Later, when the greater part of the cadmium had been deposited, the current-strength was increased until finally the eight storage cells used as the source of electricity were short-circuited through the cell. The whole operation ex-



tended over about eight hours. At the end chlorine had nearly ceased to be evolved at the anode, although some residual conductivity remained, owing to the formation of a small amount of perchloric acid. Toward the end of the electrolysis the column of bulbs and the walls of the cell were several times rinsed into the cell. At the completion of the electrolysis the electrolyte was displaced with water which had been freshly saturated with hydrogen; and the water in turn was displaced with pure alcohol, the maximum voltage being maintained between the electrodes during the operations, and care being taken not to break the electrolytic circuit. The cell was then placed in a desiccator containing fused potassium hydroxide, the pressure in the desiccator was reduced to a few millimeters of mercury with a mechanical pump, and the cell was allowed to stand until the alcohol had evaporated. The cell was next transferred to a second desiccator which contained the counterpoise of the cell, and the two were allowed to stand in a low vacuum for some hours before being weighed. Further standing in an exhausted desiccator produced no change in weight, showing both that the cell and amalgam were dry and that the amalgam had little tendency to oxidize. The rinsings, both aqueous and alcoholic, were evaporated in a quartz dish with a very small amount of redistilled sulphuric acid; and, after transference to a weighed platinum crucible, the residue was ignited at dull redness. In this way a residue, in most cases weighing less than one milligram, was obtained which was shown to be cadmium sulphate. A correction to the weight of cadmium was applied upon this basis. Complete precipitation of the cadmium was never secured, although, according to the experience of Quinn and Hulett, no cadmium is left undeposited, even when a relatively large amount of sulphuric acid is present. The small amount of free chlorine contained in the residual electrolyte in our experiments may have been the cause of the incomplete deposition of the metal.

The weighing-bottle containing the boat and the electrolytic cell were both weighed by substitution for a counterpoise very similar in construction and of the same total volume.

The experimental data and the results calculated from them (assuming the atomic weight of chlorine to be 35.457) are shown in the accompanying table. The weights here given have been reduced to the vacuum standard by applying the following corrections for each gram of substance: cadmium chloride, + 0.000152 g, cadmium dissolved in mercury, - 0.000016 g.

It will be seen that this research has yielded a value (112.417) for the atomic weight of cadmium in very close agreement with the earlier one

(112.42) obtained by Baxter, Hines, and Frevert. In other words the determinations of the cadmium and chlorine in cadmium chloride sum up to almost exactly one hundred per cent. The disagreement of the outcome of this research with that of Quinn and Hulett's work also is marked.

ANALYSIS NUMBER	SAMPLE	GRAMS OF CdCl <sub>2</sub>	GRAMS OF Cd	RATIO Cd:Cl <sub>2</sub>	ATOMIC WEIGHT
1	A	6.08570	3.73181	1.58538	112.426
2	A	4.20489	2.57863	1.58562	112.443
3	A	5.36203	3.28817	1.58553	112.436
4	B	7.50512	4.60221	1.58538	112.426
5	B	6.71591	4.11839	1.58551	112.435
6	B	5.91556	3.62763	1.58555	112.438
7	C	5.49323	3.36805	1.58483	112.387
8	B	3.14416	1.92791	1.58513	112.408
9	C	7.58705	4.65173	1.58474	112.381
10	B	2.26738	1.39006	1.58444	112.359
11	B	5.93501	3.63962	1.58562	112.443
12	F	6.04122	3.70490	1.58578	112.454
13	D	4.07400	2.49821	1.58537	112.425
14	E	9.00004	5.51879	1.58529	112.419
15	G	6.56891	4.02808	1.58534	112.423
16	G	7.12956	4.37174	1.58522	112.414
17	E	8.57291	5.25679	1.58522	112.415
18	G	7.76294	4.76011	1.58521	112.413
Average.....				1.58529	112.419
Average of analyses 14 to 18.....				1.58526	112.417

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<sup>1</sup> *J. Phys. Chem.*, **15**, 1579 (1911); *Trans. Amer. Electrochem. Soc.*, **22**, 385 (1913); *J. Phys. Chem.*, **17**, 780 (1913).

<sup>2</sup> *J. Amer. Chem. Soc.*, **27**, 222 (1905); **28**, 770 (1906).

<sup>3</sup> Richards and Parker, *Proc. Amer. Acad.*, **32**, 59 (1896).